

Response to comments of reviewers

We have responded to all of the reviewers comments. The reviewer's comments have been italicized.

Reviewer 1

In this work, the authors present an approach to model secondary organic aerosol that is thought to be formed from low-volatility organic emissions. Here they apply the methodology to model SOA formation from oxidation of aircraft exhaust, incorporating relevant oxidation mechanisms, such as multigenerational oxidation, and employing more realistic parameters. This model represents an improvement over the Robinson 2007 approach, as the authors have noted. I strongly encourage the authors place this work in better context, in order for this methodology to be effectively adopted in atmospheric models. Otherwise the manuscript overall is well written, and the approach is novel and important. Publication of this paper is recommended, after considering the following comments.

(1) The biggest concern I have is that the model parameters are very source dependent, which is a result of the difference in compounds emitted. This will imply that many different sources will need to be included into such a model (e.g. different fuel types, different engine conditions etc.), each requiring a different set of parameters $\{a_1, b_1, c_1, d_1\}$. This has not been a problem for current models, because the precursor-specific approach used currently for T-SOA allows for straightforward lumping of precursors (simply by chemical similarities). Lack of compound-specific information for the hybrid approach will not allow for that, and would make this approach very computationally expensive. However, requiring that a very complete and detailed knowledge of organic compounds for each emission source be known seems philosophically at odds with the volatility basis set approach. The authors should address this dilemma, and perhaps a balanced approach to solving this problem.

We agree with the reviewer's comment in general but would like to clarify a few things. First, we view the volatility basis set (VBS) as a framework to mathematically represent organics and not as a mechanism to model SOA. For example, one could model only T-SOA formed from a single compound using the VBS. Here, we are assuming that the reviewer is referring to volatility-based methods developed using the VBS for S/IVOC emissions. Second, it is clear from smog chamber studies that SOA formation depends on both the volatility and structure of the precursor (larger carbon number species form more SOA) (Presto et al., 2010; Tkacik et al., submitted; Lim and Ziemann, 2009a, b, 2005). In this work, we model NT-SOA formation purely as a function of precursor volatility, which we believe is a reasonable starting point since volatility is the only information available to us. Molecular structure also matters, but it may be many years before we have sufficient data on S/IVOC emissions. For aircraft exhaust, it seems that we need two different sets of parameters to model NT-SOA from aircraft engines running JP-8 presumably because of differences in molecular structure of the emissions. Finally, the volatility-based approach is not at odds with detailed speciation, but is an interim solution to model SOA from low-volatility organics until they are speciated and can be explicitly modeled.

The reviewer's point about creating many source-specific types of S/IVOC emissions is a valid concern. However, it is not clear if we expect to see the same behavior with other combustion

sources (vehicles, biomass burning). We will answer that question explicitly in future publications as more source-specific SOA data become available. In a forthcoming paper, we present SOA data from a large number of sources and propose a simple extension of the model that overcomes this problem.

We have added the following discussion to Section 5: “They Hybrid method leverages volatility information of the emissions to model NT-SOA from unspciated low-volatility organics. It is clear from smog chamber studies that SOA formation is a function not only of the volatility of the precursor but also its molecular structure (e.g. aromatics form more SOA than similar volatility alkanes). Although some progress has been made (Isaacman et al., 2012), it may be many years before we are able to study the molecular structure of emissions and develop models that account for it. Until then, one can think of the volatility-based method developed in this work as an interim solution to model SOA from low-volatility organics.

In this work, we need two different sets of parameters to model NT-SOA from aircraft engines running JP8 and it seems probable that additional parameters may be needed for aircraft engines running on FT. This implies that volatility alone is insufficient in describing the potential of the exhaust to form SOA. One potential consequence of this is that the Hybrid method may require each source would need to be treated separately, which could complicate its implementation. However, it is unclear if this will apply to emissions from other combustion sources (e.g. vehicle exhaust, biomass burning). This is an area for future research.”

(2) In section 4.3.2, the authors stated that the parameters were determined for each experiment individually. I am concerned about the robustness of these parameters, since they are semi-empirical. How do the parameters vary in the different JP8-Idle experiments? The authors should investigate if some of the parameters are in fact coupled (i.e. multiple combinations for the parameters can give the same overall aerosol concentration). This is very important in assessing if these parameters can be applied universally.

Robustness or uniqueness is a problem when fitting any SOA experiment using the VBS or two-product approach. We have tried to reduce the robustness problem by reducing the number of free parameters to 4 (the same as a two-product model). Here, the tools (fitting routines) we have used to determine the parameters are the same as those we have previously used to parameterize SOA formation from single-component species like toluene, alpha-pinene, isoprene etc. Yes, the parameters differ slightly between the different JP8-Idle experiments. But we are less concerned about the parameters presented in Table 3 since they have been derived using all the JP8-Idle experiments and therefore are less sensitive to the robustness/uniqueness issue (akin to using different experiments to parameterize SOA formation from a single species like toluene).

(3) Another issue I would like the authors to address is: does this approach only apply for fossil fuel combustion emissions? Using the same set of stoichiometric yields $\{a_1, b_1, c_1, d_1\}$ for all volatility bins is justified if compounds in different volatility bins are chemically similar (branched, cyclic, straight-chain alkanes), which is true for fossil fuels. But it might not apply for other sources, such as biomass burning. A brief discussion on how to deal with other types of emissions would be very helpful for a modeller who wants to adopt this approach.

This point is closely related to the reviewer's first comment. We agree that molecular structure matters but we do not have the analytical techniques to characterize the molecular structure of S/IVOC. Therefore, in this work, NT-SOA formation is modeled purely as a function of the precursor's volatility because that is the only information available to us. We believe that this approach should explain a reasonable amount of the variability. If it was available, composition information would likely improve the fits as different classes of compounds (branched vs. cyclic) have different yields for the same volatility.

Emissions might vary significantly across combustion sources (fossil fuel exhaust versus biomass burning emission), but it is possible that the SOA formation is most sensitive to the volatility of the precursor's emissions. Since there is very little composition information available and the modeling is semi-empirical, it would be hard to offer recommendations to model emissions from other sources. We are currently working on a paper with data from multiple sources that explicitly addresses this issue, but it is outside the scope of this manuscript.

(4) Introduction: A definition of SVOC and IVOC in terms of their C would be helpful.*

We added the following line to the introduction: "SVOCs refer to organic species that have an effective saturation concentration (C*) between 1 and $10^3 \mu\text{g m}^{-3}$ and IVOCs refer to species that have C* values between 10^4 and $10^7 \mu\text{g m}^{-3}$."

(5) pg. 9947 ln 23: Instead of "defined", the authors should use "classified" or "denoted"

"Defined" changed to "denoted".

(6) pg. 9948 ln 22: Please provide a reference that suggests the UCM is mostly branched/cyclic alkanes

We have added the references Schauer et al. ES&T, 1999, Robinson et al., Science, 2007, Robinson et al., JAWMA, 2010 and Isaacman et al., Analytical Chemistry, 2012.

(7) pg. 9948 ln 22: I don't understand the criticism about using naphthalene as a surrogate for IVOC. Naphthalene is expected to produce more SOA than alkanes of the same vapor pressure or carbon number, which would imply any estimates would be an overestimation. But in Pye and Seinfeld (2010), scaling up from naphthalene still does not make IVOC a significant SOA precursor globally, and this work shows that IVOC as the dominant precursor. I think the problem is that emissions of IVOCs are significantly underestimated.

We believe naphthalene is not the best surrogate to model IVOC for two reasons. One, the vast majority of the IVOC UCM is probably constituted of branched and cyclic alkanes that might have very different (probably lower) SOA yields than naphthalene (Robinson et al.,

2007;Isaacman et al., 2012;Robinson et al., 2010;Schauer et al., 1999). And two, as the reviewer mentioned, the use of naphthalene as a surrogate likely underestimates IVOC emissions.

(8) pg. 9950 ln 24-25: *While there can be different oxidation pathways, Heald et al. (2010) shows that on average the O/C and H/C ratios seem to follow the addition of acid group. Do the fitted parameters show a similar trend?*

The Hybrid model does not explicitly predict the composition of SOA. The paper does present a simple calculation to estimate composition for the Robinson-2007 approach to illustrate that it creates SOA that is much more oxidized than the SOA formed in the experiments.

(9) pg. 9965 ln 19-21: *Technically that is not true. There is no experimental evidence in this work showing that SOA is in fact from IVOCs, but rather the authors postulated that all the unexplained SOA comes from POCs and proceeded to build a framework to model their production.*

We agree with the reviewer but one could make that argument about any compound. How do we know that toluene is making SOA in our experiments? Because single component chamber experiments demonstrate that toluene makes SOA? Unless one measures products of the precursor in the SOA one cannot be 100% sure.

Our feeling is that this paper presents multiple pieces of evidence that S/IVOCs are contributing significant amounts of SOA. First, traditional SOA precursors (speciated VOCs) cannot explain the measured SOA. Second, single component experiments demonstrate that individual IVOCs such as branched, cyclic and straight alkanes can make SOA (Lim and Ziemann, 2009a, b; Tkacik et al., 2012; Presto et al., 2010; Presto et al., 2009). Third, the Tenax measurements demonstrate that there is substantial amount of S/IVOCs in the chamber. Finally, the yields estimated using reasonable reaction rates are plausible, which suggests that the mass balance basically works. Therefore, many of the pieces of the puzzle seem to fit together – however we agree with the reviewer that this does not prove our hypothesis. Accordingly, we have revised the text in Section 5 as follows: “We applied the Hybrid method to model SOA data from smog chamber experiments conducted on diluted aircraft exhaust. First, based on evidence that speciated VOCs accounted for less than half of the measured SOA, Tenax measurements demonstrated substantial presence of S/IVOC emissions and NT-SOA yields estimated using reasonable reaction rates are plausible, we propose that S/IVOCs are responsible for the remaining SOA and therefore are important SOA precursors in aircraft exhaust.”

(10) pg. 9974 Table 2: *The last 2 rows appear to be the same. Maybe there is a mistake?*

It is not a mistake. The following text has been added to the manuscript “Further, they found that the chromatogram for all ground-idle emissions appeared to peak near a C^* of $10^6 \mu\text{g m}^{-3}$ implying that there were considerable emissions of species with a C^* greater than $10^6 \mu\text{g m}^{-3}$ that could not be quantified but were entirely capable of forming SOA. To ensure the inclusion of all

low volatility organics that are capable of forming SOA, we assume that the mass of emissions in the $C^*=10^7 \mu\text{g m}^{-3}$ bin equals the mass in the $C^*=10^6 \mu\text{g m}^{-3}$ bin for all the ground-idle experiments.”

(11) pg. 9981 *Fig. 6: Some of the trends in SOA data look strange (e.g. FT-Idle), where there are sudden changes in measured SOA growth. Is that an artifact of the wall loss correction?*

No, it is not an artifact of wall-loss correction. The SOA production varies smoothly in time. However, in Figure 6 (now Figure 7) we plot these changes on an OH exposure basis. For some experiments we only had intermittent measurements (e.g. 8 per experiment) of the OH tracers and therefore made piecewise OH concentration estimates. A consequence is that there are step changes in the OH exposure which causes kinks in the SOA production. We have added the following statement to the figure caption: “For some experiments, OH concentrations are calculated using intermittent measurements which results in step changes in the OH exposure. For those experiments, we see sudden changes in SOA formation with OH exposure.”

(12) *In multiple occasions, the authors compared the SOA yields of branched alkanes and n-alkanes, but it is unclear whether they are comparing yields of branched alkanes to those of n-alkanes *of the same carbon number*, or *of the same vapor pressure*. This is an important distinction to make, as the volatility bins are based on vapor pressures, whereas comparing branched to straight-chain alkanes imply they are of the same carbon number.*

In the text, we are comparing SOA yields between branched and straight alkanes for the same vapor pressure. We compare the estimated yields for different VBS bins to straight alkanes with the same volatility. The goal is to evaluate whether the yields are reasonable. If the estimated yield is higher than the *n*-alkane then we postulate that the bin must contain more cyclic alkanes or aromatics; if it is lower than the *n*-alkane then we postulate the bin must contain more branched alkanes.

Reviewer 2

(1) Jathar et al. present an important extension of the typical volatility basis set (VBS) modeling framework, effectively merging “traditional” SOA yield approaches with an multi-generational approach in a new “Hybrid” approach. In this manner, SOA formation from “traditional” (T) precursors and “non- traditional” (NT) precursors can be treated within a similar framework, which is very important if we are to quantitatively understand the contributions of these different SOA precursors to the total SOA burden through the use of models. They test this framework through consideration of photooxidation experiments that use aircraft exhaust. Through their analysis they find that oxidation of NT precursors can essentially be represented through the “traditional” (yield based) framework, with only a small need to account for additional oxidation reactions (multi-generational ageing). This finding, however, is strongly tied to the particulars of their model formulation and ageing timescale. The development of this “Hybrid” method represents a useful advance over the previous method(s). However, I find that all of the discussion surrounding the particular details of the various experiment types/fuel types distracts from the main point of the paper. I believe that revision to provide a stronger focus on the main paper motivation (development of the Hybrid model) would be beneficial. Further, I find that some key aspects of the model formulation are not clear in terms of the actual implementation (as opposed to conceptual picture, which is clear), making it somewhat difficult to understand the final results. Also, it is not entirely clear whether the authors are developing the Hybrid approach as a more physically-based representation of SOA formation from NT precursors (and T-precursors, as well) or whether the primary motivation is simply better fitting of data. If the former, I have concerns about the particular details of their model formulation and interpretation of their results in terms of physical mechanisms, which are elaborated upon below. If the latter, the authors have succeeded reasonably well. Although I believe that the Hybrid approach represents an important advance in the field, I believe that some key aspects must be clarified before this manuscript is publishable.

The reviewer makes good points, many of which are elaborated below. The overall goal of this paper is to develop an improved framework for simulating SOA from S/IVOCs. It is a semi-empirical approach that is quite similar to what has been developed for traditional SOA formed from VOCs. The approach is informed by our understanding of the chemistry of the system (i.e. the underlying equations represent the chemistry), but ultimately the parameters for the model are determined by fitting the data and by underlying assumptions. We believe that the approach has a firmer physical basis than Robinson-2007 but it is still semi-empirical.

We argue that the Robinson-2007 method to model NT-SOA formation is deficient because it assumes an unrealistically modest change in the volatility of the precursor with every oxidation reaction. By building a Hybrid method that allows for much larger changes in volatility with products spread across the volatility scale, we have created a model that is more physically realistic that also fits the data better. From that we conclude that the Hybrid method is more representative of SOA formation from S/IVOC than the Robinson-2007 method. As for the exact mechanisms that lead to SOA formation, it would be hard to say anything at this point considering that the composition of S/IVOCs still remain poorly constrained.

We have addressed the reviewer’s point about a stronger focus on the Hybrid method by

significantly revising the opening paragraphs in the ‘Abstract’ and ‘Conclusions and discussion’.

(2) Eqn. 4: It seems inconsistent to me to allow the 2nd and later generation T-SOA and NT-SOA products to only undergo a 1 order of magnitude reduction in volatility while the production of 1st generation products occurs as a distribution. If the first generation of oxidation can produce products with distributions of volatility, why can't the nth-generation of oxidation do the same? Is this distinction made simply to allow for computational efficiency and to keep the number of required parameters smaller than it might otherwise be?

We agree with the reviewer's point. Later generations of oxidation will certainly make a distribution of products. However, we have chosen to represent it more simply (one product) for three reasons. One, smog chamber experiments used in this work and elsewhere do not expose the emissions to multiple generations of oxidation (low OH exposure and products assumed to have lower reactivity than products), i.e. the SOA in the chamber is mainly first generation SOA. Two, there are no experimental data to constrain the product distributions associated with multi-generational oxidation. And three, it is unlikely that future generations of oxidation behave similar to the first generation of oxidation based on recent work that shows fragmentation to increase with oxygenation of the molecule.

We have largely included the aging term in the model for completeness. We believe it is critical and want to emphasize that one cannot assume the products are stable and non-reactive.

To clarify the discussion about first and multi-generational oxidation, we have added the following text to the manuscript: “Application of the NT-SOA model (equation (3)) requires differentiating between first and later generation oxidation products. In the context of this paper, the term “first generation” refers to the first set of stable products that arise after a series of oxidation reactions (Lim and Ziemann, 2005). The term “multi generation” refers to the continued oxidation of the stable first-generation products. However, cleanly differentiating between the first and later generations of products is difficult in photo-oxidation experiments. In this paper, we empirically differentiate between first and later generation of oxidation production by assuming that the SOA formed during a typical 3 to 4 hour smog chamber experiment is dominated by the first generation of oxidation. This seems like a reasonable assumption because these experiments typically have aggregate hydroxyl radical exposures of 10^7 molecules hr cm⁻³, which creates about one e-fold of oxidation for precursors with typical S/IVOC reaction rate constants (Atkinson and Arey, 2003). This assumption breaks down in systems in which later generation products are significantly more reactive than the original precursors.

Based on our definition of first-generation (inside the smog chamber) and multi-generational (beyond the smog chamber) oxidation, theoretically we do not need to run the multi-generational oxidation mechanism while modeling SOA in the smog chamber. But doing so would incorrectly imply that the oxidation products formed in the smog chamber were non-reactive. Hence, for the sake of completeness (but at the cost of not being true to our definitions), we let the oxidation products that are formed in the smog chamber to undergo multi-generational oxidation.”

(3) *Eqn. 6: If I am reading the matrix shown in Eqn. 6 correctly, this indicates that the 4 products that are produced as first generation products span 4 orders of magnitude (which makes sense based on addition of ketones, alcohols and carboxylic acids, which span 4 orders of magnitude of volatility). However, it appears that the highest volatility species in this array of products has a volatility that is reduced by 3 orders of magnitude from the parent species. This means that the actual reduction in volatility, relative to the parent species, ranges from 3-6 orders of magnitude, which seems too large to me. A range of 1-4 orders of magnitude seems more reasonable to me, based on addition of ketones, alcohols and carboxylic acids (see Pankow and Asher, 2008). As such, whereas the Robinson et al. (2007) formulation might underestimate the decrease in volatility per reaction, it seems as if the Hybrid method is over-estimating. This said, I am open to the idea that I am completely misinterpreting how the Hybrid method is actually being implemented because I am having some difficulty reconciling what is shown in Table 3 with Eqn. 6 (see comment below regarding Table 3).*

The reviewer is reading equation 6 correctly. To explain the amount of SOA formed in the chamber the volatility of the S/IVOCs must be reduced by 3 to 6 orders of magnitude. As pointed out by the reviewer, this is greater than the reduction associated with the addition of a single functional group. It is similar to reductions in volatility that must occur to make SOA from VOCs. The only explanation is that the products forming SOA are the result of a series of reactions that add multiple functional groups. It is this series that gives rise to our empirically defined “first generation” of products.

Further, rather than just looking at the total range, it would be more appropriate to calculate the average reduction in C^* for the products. For that, we calculate a mass-yield weighted C^* which represents the average reduction in C^* of the product compared to its precursor. The average reduction remains the same for all precursors in an experiment since each precursor forms the same volatility distribution of products that are simply shifted in volatility space. For the final set of ground-idle and ground-non-idle yields (Table 3), the average products seems to be between 3 and 4 C^* bins or 3 to 4 orders of magnitude lower than the precursor.

To clarify, we have added the following text to section 2.2.2 that includes equation (6): “To determine the mass-yield matrix, we assume that each precursor undergoes several oxidation reactions in the smog chamber before it forms a stable set of products. Hence, we expect the particle-phase oxidation products to be much less volatile compared to its precursor. For a VOC like toluene ($C^* \sim 1.6 \times 10^8 \mu\text{g m}^{-3}$), Hildebrandt et al. (2009) observed that the products of oxidation were centered around the $C^*=100$ and $C^*=1000 \mu\text{g m}^{-3}$ bins, i.e. most of the products were 5 to 6 orders of magnitude lower than the precursor (toluene). Tkacik et al. (2012) observed that most of the measurable photo-oxidation products of cycloalkanes and branched alkanes were 3 to 6 orders of magnitude lower in volatility than their precursor. Serving as our guide, we assume that in the Hybrid method, a precursor is allowed to form oxidation products that are 3 to 6 orders of magnitude lower in volatility than the precursor.”

(4) *The combination of (1) allowing reactions of the initial precursors to form a distribution of species (over 4 orders of magnitude in volatility) while reactions of later generation species only reduce volatility by 1 order of magnitude and (2) the excessively large reduction in volatility (3-6*

orders of magnitude) for products of initial precursors will inevitably make it such that the model is biased towards SOA formation from 1st generation products. Thus, it is not surprising that the authors find that the 1st- generation NT-SOA dominates the SOA mass (see Figure 6). Although this model formulation may fit the observed SOA formation with reasonable fidelity, interpretations (such as those in Section 4.3.2 and Section 5) in terms of physical meaning based on the model results are questionable.

We agree that the model is structured such that “first-generation” products explain most of the SOA. Both of the reviewer’s concerns have been discussed and addressed in the response to the previous comments. In comment #2, we discussed why the reduction in volatility is different between the first and future generations of oxidation. In comment #3, we argued why a 3 to 6 order of magnitude reduction in volatility was justified.

We agree with the reviewer that using the above argument to make claims about any physical meaning are speculative. We have changed the text in Section 4.3.2 to: “Figure 9(a) shows that the estimated SOA yields for IVOC in the 10^5 , 10^6 and 10^7 $\mu\text{g m}^{-3}$ bins (symbols) are equal or higher than published yields for *n*-alkanes in the same C* range (dashed lines; $\text{C}_{14} \sim 10^5$ $\mu\text{g m}^{-3}$, $\text{C}_{12} \sim 10^6$ $\mu\text{g m}^{-3}$ and $\text{C}_{10} \sim 10^7$ $\mu\text{g m}^{-3}$). We believe that the higher yields are due to unburned fuel being a large component of the ground-idle emissions (Presto et al., 2011) and JP8 fuel is dominated by cycloalkanes and aromatics which have higher SOA yields than *n*-alkanes. In contrast, Figure 9(b) shows that the effective SOA yields for S/IVOC in the 10^3 and 10^4 $\mu\text{g m}^{-3}$ bins (symbols) are lower than the published yields for *n*-alkanes (Presto et al., 2010) in the same C* range (dashed lines; $\text{C}_{18} \sim 10^3$ $\mu\text{g m}^{-3}$ and $\text{C}_{16} \sim 10^4$ $\mu\text{g m}^{-3}$). Similarly, we hypothesize that S/IVOC emissions during non-ground-idle conditions are dominated by species that have lower SOA yields than similar volatility *n*-alkanes such as branched alkanes or carbonyls (Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010).”.

(5) Table 3: (1) This table should be mentioned in Section 4.3.2, not just in the conclusions. (2) I have a very difficult time understanding this table, and this lack of understanding arises due to some confusion on my part regarding how exactly the Hybrid method is being implemented. The authors’ state that in order to reduce the number of parameters in their model from 40 to 4 they will assume that upon reaction there is “the same product distribution arising from each POC precursor, but shifted in volatility space by one order of magnitude” (P9955). I interpret this to mean that there is but one set $[a_1, b_1, c_1, d_1]$ that is adjusted to fit the Hybrid model to the observations for a given experiment, and not a different parameter set for each precursor (i.e. bin of the VBS). Further, based on Eqn. 6 I interpret this to mean that these parameter sets will correspond to different C product ranges with the range dependent upon the volatility of the parent species. Table 3 makes it appear as if reactions of all POC species, no matter their C*, lead to production of species with C* values ranging from 10^0 to 10^3 $\mu\text{g m}^{-3}$. This seems highly inconsistent with what is shown in Eqn. 6. Further, in Table 3 POC species with varying C* values are listed as having different parameter sets. Shouldn’t there be one $[a_1, b_1, c_1, d_1]$ set for each experiment (engine/fuel combination) and not for each POC C* value? Perhaps I am misunderstanding, but I find the manuscript to not be clear on these points.*

We have added Table 3 to Section 4.3.2. Based on the reviewer's comments, we have also made the table very simple to understand using the matrix (equation 6) and notations ($[a_1 \ b_1 \ c_1 \ d_1]$) defined earlier.

Table 3: VBS yields for S/IVOC for ground-idle and non-ground-idle emissions.

Ground Idle Yields				Non-Ground Idle Yields			
a_1	b_1	c_1	d_1	a_1	b_1	c_1	d_1
0.00	0.10	0.10	0.20	0.05	0.10	0.00	0.00

(6) Most of the experiments took place at OH exposures $< 1 \times 10^7$ molecules-hr cm^{-3} . For a C_{15} (for example) hydrocarbon, this corresponds to < 1 oxidation lifetime. (Of course, the specific relationship between exposure and oxidation lifetimes really depends on specific distribution of precursor compounds. However, I think that the idea expressed here is generally applicable.) In fact, one oxidation lifetime is not reached until the OH exposure is $\sim 1.5 \times 10^7$ molecules-hr cm^{-3} . Only a few experiments go beyond this level of exposure. Given this, it is not surprising that the authors find that the SOA is dominated by 1^{st} -generation products. It is not clear to me that the experiments the authors compare/fit their Hybrid model with are really the best choice for the development of the model.

The reviewer raises a valid point that the experiments have been conducted at very low OH exposures or in other words, the experiments represent a short time span of the oxidation of the emissions. This is part of the reason why we have a first-generation heavy model. It also means that the data provide relatively little constraint on multi-generational oxidation. As discussed in the response to comment #2, we include multi-generational oxidation in the model because we believe that it is important in the atmosphere (but not necessarily in these experiments).

We chose this dataset mostly because these are the only set of experiments conducted on combustion emissions that we know of, where SOA and its high- and low-volatility precursors were systematically characterized. Robinson et al. (2007) and Grieshop et al. (2009a, b) measured SOA formation from diesel exhaust and wood smoke respectively but only measured light-aromatic SOA precursors. Chirico et al. (2009) and Heringa et al. (2010) measured SOA formation from diesel exhaust and wood smoke respectively but did not seem to measure any SOA precursors.

In regards to the OH exposure, the levels achieved in these experiments are slightly less than those typically achieved in other smog chamber experiments run at Carnegie Mellon University (Chacon-Madrid et al., 2010; Grieshop et al., 2009; Hildebrandt et al., 2009; Miracolo et al., 2011; Miracolo et al., 2010; Presto et al., 2010; Presto et al., 2009; Tkacik et al., 2012). Running higher OH exposure experiments would necessitate the use of OH precursors like hydrogen peroxide or nitrous acid, which could influence the traditional pathways of SOA formation and confound results. Further, higher OH exposures could also mean that the experiments would need to be run longer in bigger chambers, which would add significant uncertainty from wall-losses in calculating SOA formation.

(7) P9947/L14 (and throughout): *I find the terminology POC a bit odd in the context of IVOC's and SVOC's. I have typically interpreted "primary" to indicate "particles that are directly emitted" from sources. Although this may be the ultimate source of IVOC's and SVOC's, it then seems strange to refer to "POC vapors," since the "vapor" aspect indicates that the species is no-longer "primary". Yes, this is purely semantics, but I feel that more precise terminology would be helpful to the community. Along these same lines, eventually the distinction between "traditional" and "non-traditional" SOA will need to be dropped, as what is currently "non-traditional" will become part of the "traditional" hierarchy. Perhaps now is the time to introduce new, exquisitely precise terminology?*

We have removed POC and POC vapors from the manuscript and replaced it with S/IVOC. We have decided to retain the NT-SOA terminology.

(8) P9947/L26: *Certainly some of the emitted species are not branched or cyclic?*

We have changed the sentence to: "Instead they are classified as an unresolved complex mixture (UCM) that is thought to be dominated by co-eluting branched and cyclic alkanes (Robinson et al., 2007; Isaacman et al., 2012; Robinson et al., 2010; Schauer et al., 1999)."

(9) P9948/L18: *Was the Robinson (2007) method really "fit" to measured SOA formation? I know that the volatility distribution of the POA was fit to observations, but was the method that involves allowing the gas-phase species to react actually explicitly fit to data? My reading of the Robinson et al. (2007) paper (including the SOM) gives no indication that the method was "fit" to measured SOA formation, although in a later paper Shrivastava et al. (2008) compare the Robinson et al. (2007) method to chamber data and demonstrate reasonable agreement (although the Shrivastava et al. comparison does not appear to have been truly a "fit" either). Perhaps this is just some confusion on my part as to what the authors specifically mean by "method"? I am interpreting "method" as the ageing scheme, per the first sentence of their previous paragraph. Further, it seems to me that the Pye and Seinfeld (2010) method is just as constrained as the Robinson et al. (2007) method; that is, neither is explicitly constrained through "fitting". Although it may not have been the authors intention, as written it sounds as if the authors are criticizing Pye and Seinfeld for this lack of laboratory constraints even though I would argue that the exact same criticisms apply to the Robinson et al. method. I suggest re-phrasing.*

We certainly are not criticizing the Pye and Seinfeld method. Neither method is based on fitting the data like traditional SOA models. The reviewer has made a valid point and we have changed the text accordingly to: "However, there are several shortcomings with existing methods to model NT-SOA formation. First, the parameters for those methods are based on very limited experimental data. In particular the methods are not based on explicit fitting of experimental data like what is done for traditional SOA. Shrivastava et al. (2008) showed that the parameters used in Robinson et al. (2007) were able to reasonably predict the measured SOA formation from diesel exhaust; it has been assumed that the same fits can be used to model all emissions (fossil

fuel, bio fuel and biomass burning) (Shrivastava et al., 2008;Jathar et al., 2011). Further, Pye and Seinfeld (2010) used naphthalene as a surrogate for all unspciated IVOCs even though these are thought to be mainly branched and cyclic alkanes (Robinson et al., 2007;Isaacman et al., 2012;Robinson et al., 2010;Schauer et al., 1999).”

(10) P9948/L26: *It is not clear to me what the authors are getting at by pointing out that IVOC emissions are inferred from “other source test”. Some elaboration on this point would be appreciated.*

To be more clear, we have changed the sentence as follows: “Third, the IVOC emissions were not directly measured. For the Robinson-2007 method they were estimated by scaling POA based on the work of Schauer et al. (1999, 2001, 2002); for the Pye and Seinfeld (2010) method they were estimated by scaling naphthalene emissions.”

(11) P9949/L6: *The authors state that a limitation of smog chamber experiments is that they only capture the evolution of “the first few generations of oxidation”, which only captures “5-10% of the time spent by precursors and their products in the atmosphere”. Although this may be true, it seems a bit misleading to me in that after “a few” (which I will take to mean 3 or more) generations, the precursor will have decayed to $\exp(-3) = 5\%$ of its initial concentration. This is then more like 95% of the “time spent” by the precursors in the atmosphere. True, the products may be around a bit longer, but they will also decay within “a few” lifetimes.*

To be clearer, we have changed the sentence to: “A limitation of smog chamber experiments is their limited oxidant exposure; they only capture, at most, the atmospheric evolution of the first generation or two of oxidation of the precursors and their immediate products.”

(12) P9949/L8: *If the authors are truly only focusing on “the first generation” of oxidation, then I do not understand the motivation for the development of the “hybrid” method. Shouldn’t application of the “traditional” approach work if there is truly only one generation? Some clarification would be appreciated.*

This is a reasonable point. The Hybrid method, as applied in this paper, mainly focuses on the first generation of oxidation. In the atmosphere, later generations will likely play an important role in the SOA formation. Therefore we want to make sure that multi-generational oxidation was explicitly included in the formalism. We limit our modeling to first generation of products because that is what a typical smog chamber is able to capture. That does not mean that multiple generations are unimportant.

(13) P9952/Section 2.1: *A terminology question. The T-SOA (= traditional SOA) method typically assumes that the products are unreactive. In the hybrid model, products are reactive to OH. Are the products of these reactions then classified as NT-SOA, even if the original precursor was a “T” precursor? Or are they still T-SOA? Also (and more importantly) doesn’t allowing*

the gas-phase products to continue to react preclude the use of the original T-SOA formalism, since the yields were derived under the assumption that the products were unreactive even though they may have actually been reactive? In other words, don't T-SOA yields in some crude way include reaction of products (although perhaps not in an accurate manner), which means that allowing gas-phase species in the T-SOA framework could be double counting? I say "could be" because I think that this will depend on how the yields were measured. If yields were measured after allowing the precursor to react over many lifetimes of oxidation, then oxidation of products is important. But if yields were measured after <1 lifetime, then oxidation of products is not as important and the measured yield may not include further oxidation of products. Could it be that the studies with higher yields tend to be those that have gone through more lifetimes of oxidation?

We understand that T-SOA has been defined by prior studies as the non-reactive, stable oxidation product of speciated SOA precursors. In this work, they undergo multigenerational oxidation as mentioned in the second paragraph in Section 2.1 and the multi-generational products of T-SOA are still classified as T-SOA. To clarify this new definition in the manuscript, we have added the following sentence to Section 2.1: "Previously, T-SOA has been defined as the non-reactive, stable oxidation product of traditional SOA precursors. In this work, we define T-SOA as the first and multi-generational SOA mass arising through the oxidation of speciated VOC precursors."

The concerns raised by the reviewer are valid and illustrates general problems with the SOA yield methodology. However, they are too specific and beyond the scope of this work to be addressed in this manuscript.

(14) *P9957/L1: I suggest that for the papers that are not published the authors indicate them as, e.g., Drozd et al. (in preparation) instead of Drozd et al. (2012).*

Drozd et al., 2012 has since been published and updated in the bibliography.

(15) *Figure S1: I recommend moving this figure to the main text.*

Figure S.1 moved to the main text.

(16) *Table 2: It could be useful if the authors were to indicate the C^* values for the VOC's, so that the initial volatility of species can be understood in the context of the volatilities of the POC species. For example, undecane has a $C^* \sim 10^7 \text{ ug m}^{-3}$, giving it a volatility close to the highest volatility bin of the POC. This, in some ways, raises the broader question of what is a "traditional" precursor and what is a "non- traditional" precursor in the context of the VBS (which ultimately defines compounds according to their volatility, not their identity). If these species overlap in volatility (i.e. end up in the same bin), are they distinguishable?*

We have added C^* of the VOCs to Table 2.

In this work, we define a “traditional” precursor as emissions that can be speciated and a “non-traditional” precursor as emissions that cannot be readily speciated. It just so happens that most of the traditional precursors (measured using conventional GC-MS techniques) have a C^* greater than or equal to $10^6 \mu\text{g m}^{-3}$ and the non-traditional precursors (measured using a TD-GC-MS) have a C^* less than or equal to $10^7 \mu\text{g m}^{-3}$. We might be double counting some precursors but given that a very small fraction of the non-traditional precursors can be speciated, our results are not very sensitive to the double counting.

(17) Section 3.4: *It is not clear whether the authors used, in their modeling, an average [OH] or a time varying OH. If [OH] varies significantly throughout the experiment, this could have a dramatic influence on the model performance. This, I believe, to be very important and requires clarification.*

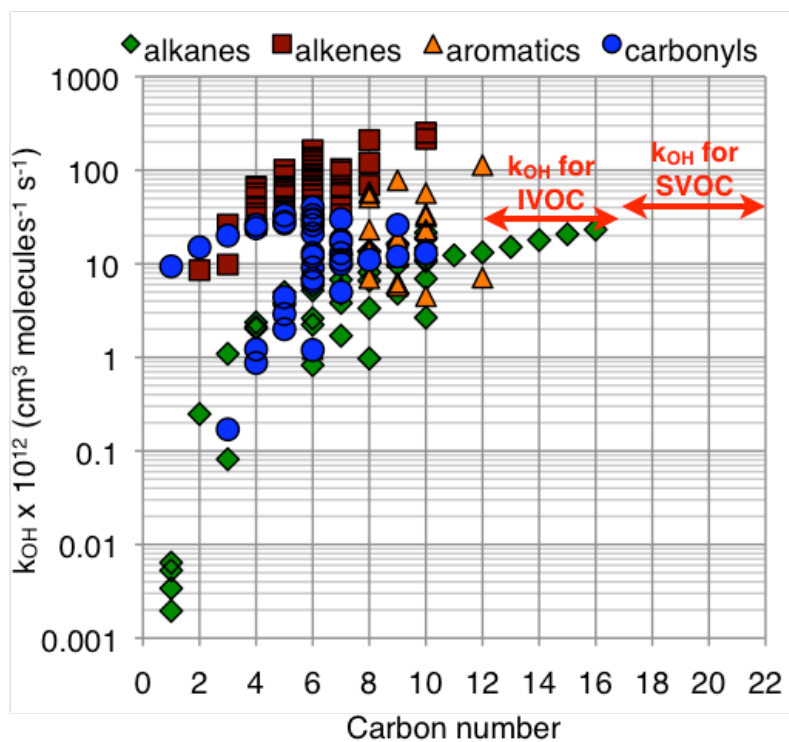
The OH concentrations are calculated from time-resolved decay of inorganic and organic species. Hence, the OH concentrations used in our analysis are time dependent. To make that clear, we have added the following text to the manuscript in Section 3.4: “The OH concentration varied with time; it was about 10^7 molecules cm^{-3} at the beginning of the experiment and dropped to 10^6 molecules cm^{-3} by the end. This time variation was accounted for in the modeling.”

(18) P9960/L5: *I missed the fractional error values in Figure 4 at first due to the large density of gridlines. I suggest using just major gridlines.*

We have removed the gridlines to make the fractional error values more visible.

(19) P9960/L19: *The authors should justify the change in rate coefficient for the higher vs. lower volatility species. Presumably they are accounting for differences in the size of the molecules (which makes sense), but then why not use a k_{OH} that varies with $\log C^*$? Why a step function and what are the implications of using a step function?*

We decided to just have two reaction rates (one for IVOC and one for SVOC) for simplicity. The figure below plots the k_{OH} for numerous alkanes, alkenes, aromatics and carbonyls listed in Atkinson and Arey (2003) as a function of carbon number. SVOC and IVOC are at the low end of these data. In our work, the k_{OH} for SVOC and IVOC are based on the extrapolated lower bound *n*-alkane data. For higher carbon number (or lower volatility) species, the k_{OH} is a much stronger function of molecular structure than carbon number. Therefore, a k_{OH} as a function of carbon number or volatility would not have a strong effect on our results.



(20) P9961/L9: The authors state that NT-SOA yields increase with increasing C_{OA} . However, this appears to be the case only for some of the aerosol types, not all. Can the authors comment? Perhaps this statement should be revised to say that NT-SOA yields increase for some, but not all species?

We have changed the text as follows: “Finally in most experiments, the NT-SOA yields increase with increasing C_{OA} , implying that the NT-SOA is semi-volatile, similar to T-SOA formed in smog chamber experiments (Odum et al., 1996).”

(21) P9962/L14: The authors need to clarify how they can have fractional values of q (which defines the number of volatility bins that a product decreases from the parent species). Presumably, they distribute mass into the different VBS bins based on a weighting scheme, but this is not clear. Or, perhaps I am misunderstanding the phrase “a range of 1 to 2” and the authors mean “either 1 or 2” with fractional values not allowed?

Yes, we mean either 1 or 2. We have changed the text accordingly.

(22) P9962/L14: It is not clear why the authors constrain the q values over the range 1-2. Why not allow larger values? Would this allow the NT-SOA model to perform better?

We constrain q to either 1 or 2 because those are values that have been used previously (1: Robinson et al. (2007), 2: Grieshop et al. (2009a)). In essence, a higher q is exactly what we

propose in the Hybrid method (in addition to a volatility distribution of products). But in the Hybrid method, we restrict the use of the “higher q ” to the first generation products because we do not have any data to suggest that we should keep using a “higher q ” for multigenerational products.

(23) P9962, Line 19: *It is not clear what the authors mean by “reproduce the SOA data.” Consideration of Figure 4b appears to indicate that, in many cases, the SOA data are not “reproduced” by the model; the NT-SOA model simply does a better job than the T-SOA model alone.*

We have replaced ‘reproduce’ with ‘fit’.

(24) P9963/L21: *The high O:C is not straight-forwardly the result of precursors having to go through multiple generations to attain low enough volatility. It is a combination of the authors q values and the f_{oxy} values. If they have sufficiently small f_{oxy} , little oxygen will be added regardless of how many generations the products go through. Similarly, if they have large q and large f_{oxy} , lots of oxygen can be added after only a few generations. The point isn’t that multiple generations are not important, only that the importance of the f_{oxy} and q terms appears to be somewhat understated here.*

We agree with the reviewer’s view but the point we are making is that for the Robinson-2007 method if q is restricted to 1 or 2, then f_{oxy} needs to be very high for the model to get the OA mass right. But a high f_{oxy} results in too high an O:C ratio. This would suggest that one cannot get both the mass and O:C right with the Robinson-2007 method.

(25) P9964/L5: *It is not clear where the upper and lower experimental bounds derive from.*

To make it clear, we have changed the sentence as follows: “The upper and lower bounds of the SOA are presented to indicate experimental uncertainty due to wall-losses (we have not accounted for uncertainty in the T-SOA model).”

(26) P9964/L9: *It is certainly interesting that the first generation products of POC dominate the NT-SOA. However, this should not be surprising given the model formulation which assumes that all POC products decrease their volatility by 3-6 orders of magnitude. As stated earlier, this seems like too large of a decrease to me (given that even carboxylic acid addition will lead to volatility decreases of only ~4 orders of magnitude), which leads to a larger attribution of the NT-SOA to 1st generation products than may actually be occurring. However, if the aim of the hybrid method is to simply better reproduce the time-evolution of the SOA formed, perhaps this is reasonable.*

On average, the products need to be 3 to 4 orders of magnitude lower in volatility than the precursor if the model is to match the temporal evolution of SOA. A 3 to 4 order of magnitude

change in volatility is plausible because the first generation of oxidation could represent several oxidation reactions and therefore the addition of multiple functional groups to the precursor.

(27) *Figure 8/P9964: It is not clear to me how the authors keep track of the SOA formed from each discrete precursor in the model. In the hybrid model, the products from the different precursors rapidly overlap given that each precursor gives rise to species that span 4 VBS bins. How do the authors keep track of which precursor formed what? Is this related to the assumption of “the same product distribution arising from each POC precursor, but shifted in volatility space by one order of magnitude” (P9955)?*

We keep track of the SOA from each C* precursor by using a different product VBS for each precursor. Although this increases the computational burden, it allows us to explicitly track the source of the SOA. However, it is not necessary to do that in a CTM since the multigenerational oxidation for all products is the same irrespective of its parent precursor.

(28) *P9965: I find this discussion relating to yields from the various precursors to be weak. Perhaps this is because I have some difficulty understanding how the yields are determined (see above comment), but also because the conclusions here are intimately tied to the particulars of the model formulation. Again, I come back to the point that the authors use a scheme in the hybrid method that assumes decreases of 3-6 orders of magnitude in volatility for the reaction of the parent compound (but only 1 order of magnitude for reaction of subsequent products). This choice will determine which species appear to contribute most to the SOA and will determine the yields from particular VBS bins. If the authors used a scheme that decreased volatilities by 1-4 orders of magnitude, I imagine that their conclusions would be altered. Thus, it seems a bit of a stretch to, at this point, firmly conclude that yields in the 10^3 - 10^4 bins are lower but yields in the 10^5 - 10^7 bins are higher than equivalent *n*-alkanes and to subsequently use this to identify (in a general sense) the chemical nature of the precursors.*

We agree with the reviewer that using the above argument to make claims about any physical meaning are purely speculative. We have changed the text in Section 4.3.2 to: “Figure 9(a) shows that the estimated SOA yields for IVOC in the 10^5 , 10^6 and 10^7 $\mu\text{g m}^{-3}$ bins (symbols) are equal or higher than published yields for *n*-alkanes in the same C* range (dashed lines; $\text{C}_{14} \sim 10^5$ $\mu\text{g m}^{-3}$, $\text{C}_{12} \sim 10^6$ $\mu\text{g m}^{-3}$ and $\text{C}_{10} \sim 10^7$ $\mu\text{g m}^{-3}$). We believe that the higher yields are due to unburned fuel being a large component of the ground-idle emissions (Presto et al., 2011) and JP8 fuel is dominated by cycloalkanes and aromatics which have higher SOA yields than *n*-alkanes. In contrast, Figure 9(b) shows that the effective SOA yields for S/IVOC in the 10^3 and 10^4 $\mu\text{g m}^{-3}$ bins (symbols) are lower than the published yields for *n*-alkanes (Presto et al., 2010) in the same C* range (dashed lines; $\text{C}_{18} \sim 10^3$ $\mu\text{g m}^{-3}$ and $\text{C}_{16} \sim 10^4$ $\mu\text{g m}^{-3}$). Similarly, we hypothesize that S/IVOC emissions during non-ground-idle conditions are dominated by species that have lower SOA yields than similar volatility *n*-alkanes such as branched alkanes or carbonyls (Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010).”.

(29) *P9964/L18: Figure 8a shows precursors with $\text{C}^* = 10^3$ and 10^4 $\mu\text{g m}^{-3}$, not $\text{C}^* = 10^2$ and*

10^3 ug m^{-3} (at least according to the labels in the figure). Panel b is similarly mislabeled.

The figure is correct. We corrected the text accordingly.

(30) P9951/L5: *It is interesting that the authors note the potential for fragmentation reactions to increase volatility, but their proposed scheme does not explicitly include any sort of accounting of this effect. Perhaps this comes out in the [a, b, c, d] array? However, it would be good if the authors would comment on how their model does/does not capture the effects of these fragmentation reactions.*

As the reviewer has pointed out, the first-generation parameters [a₁ b₁ c₁ d₁] are empirically derived and implicitly account for fragmentation. It would be too early to comment on how fragmentation needs to be modeled for multi-generational oxidation.

(31) Fig. 6: *For experiments where POA is substantial, the model indicates constant POA with time. Doesn't the POA evaporate in response to depletion of the gas-phase reservoir (see Miracolo et al., 2010)? Or is the volatility of the POA so low that this is not a concern?*

The POA does not evaporate because POA and SOA mix together and the C_{OA} increases in all experiments, which shifts the gas-particle partitioning towards the condensed phase. In fact, analysis of the AMS data indicates that in experiments in which there was substantial SOA formation (e.g. JP8 idle) the amount of POA in the chamber actually increases due to changes in gas-particle partitioning.

(32) Fig. 6: *After looking over the comments of Reviewer #1, I must agree that some of the observed behavior shown in Fig. 6 for some of the experiments is quite odd and should be commented upon.*

The SOA production varies smoothly in time. However, in Figure 6 (now Figure 7) we plot these changes on an OH exposure basis. For some experiments we only had intermittent measurements (e.g. 8 per experiment) of the OH tracers and therefore made piecewise OH concentration estimates. A consequence is that there are step changes in the OH exposure which causes kinks in the SOA production. We have added the following statement to the figure caption: "For some experiments, OH concentrations are calculated using intermittent measurements which results in step changes in the OH exposure. For those experiments, we see sudden changes in SOA formation with OH exposure."

Reviewer 3

Jathar et al. present a re-formulated approach to modeling SOA formation from IVOC and SVOC emissions (so called Non-Traditional SOA or NT-SOA). They use data obtained during two aircraft engine emissions experiments in which emissions were sampled into a portable smog chamber, oxidized via reaction with OH and analyzed – accounting for the SOA formed through traditional VOC precursors and unspeci-ated I/SVOC precursors (by subtraction). The collected data provides the empirical basis for parameterizing NT-SOA formation using a hybrid model approach. The aim of the manuscript is to describe and justify the NT-SOA parameterization. Ultimately, the authors hope that their approach will provide the basis for improved model treatment of NT-SOA formation across many different combustion processes. The scientific content of the manuscript represents an important contribution to the atmospheric community. Prior to publication in ACP, the authors should address the following points.

(1) The authors should seriously consider NOT using the terminology POC (Primary Organic Carbon) to describe I/SVOC exclusively. There are non-I/SVOC primary organic carbon emissions and as such the current terminology does not make sense and will likely lead to confusion/frustration in the wider atmospheric chemistry community.

We have removed POC from the manuscript and replaced it with S/IVOC.

(2) The authors should provide a reference at: P 9947, L25 “Instead it is classified as an unresolved complex mixture (UCM) that is thought to be a complex mixture of branched and cyclic alkanes.”. And also here: P 9948, L23 “but IVOC UCM is thought to be mainly composed of branched alkanes.”

We have added the references Schauer et al. ES&T, 1999, Robinson et al., Science, 2007, Robinson et al., JAWMA, 2010 and Isaacman et al., Analytical Chemistry, 2012.

(3) The authors need to elaborate on how the gas phase precursors and condensed phase oxidation products can have the same residence times in the atmosphere. This seems incongruous. p.9949 L5: first few generations of oxidation or about 5–10 % of the time spent by precursors and their products in the atmosphere.

Condensed and gas-phase species have different lifetimes. We have changed the sentence to: “A limitation of smog chamber experiments is their limited oxidant exposure; they only capture, at most, the atmospheric evolution of the first generation or two of oxidation of the precursors and their immediate products.”

(4) Given these limitations, the authors state that they will focus only on the first generation of oxidation quantifying this further in section 3.2 stating: “The secondary PM data were measured after three to four hours of oxidation inside the smog chamber at typical atmospheric OH concentrations.” But in section 3.4 the authors state that the inferred OH concentration suggest: “The OH exposure ranges from 4 to almost 50 h of atmospheric oxidation at a typical OH

concentration” Perhaps I am misunderstanding the scope of the current experiment – Nevertheless, the authors should clarify this confusion.

We have changed the sentence in Section 3.2 to “The secondary PM data were measured after three to four hours of oxidation inside the smog chamber.” and kept the sentence in Section 3.4.

(5) Section 3.1 It would be useful for those not familiar with aviation fuels if the authors provided the compositional differences between the JP8 and FT fuels in this section. Rather than providing this information in the conclusions.

We have added the following sentence to Section 3.1: “On a mass-basis, JP8 consists of 53% straight/cyclic alkanes, 30% branched alkanes and 17% aromatics while FT consists of 88% branched alkanes and 12% cyclic alkanes.”

(6) On P 9957, L11 the authors state: “The emissions were diluted with clean (HEPA-and activated-carbon filter) air to achieve concentration levels in the chamber that were representative of downstream of the engine exit plane.” Perhaps the authors could provide a reference or additional information that substantiates this claim. It would be useful to know what distance downwind of the engine exit plane the chamber dilution is set to mimic. Also, given that the air surrounding airports is often influenced by the other jet and non-jet combustion sources – the ‘real’ dilution environment likely has non-zero concentrations of organic aerosol. Given this consideration, it would be useful if the author could comment on the role that this airport C_{OA} would play in influencing the mass yield of NT-SOA. Also, if the chamber experiments are run over 50 h equivalent OH exposure in a 4 hour time period – the authors should comment on how their results would be influenced by this non-real-world oxidation condition. But perhaps the 50 h equivalent oxidation is not relevant for the current experiment.

To address the dilution comment, we have changed the sentence to: “The emissions were diluted 50 to 200 times with clean (HEPA- and activated-carbon filter) air to achieve primary PM concentration levels in the chamber that were representative of those typically found roughly 100-m downstream of the engine exit plane ($< 10 \mu\text{g m}^{-3}$). Photo-oxidation then increased the aerosol levels, in certain experiments to 100s of $\mu\text{g m}^{-3}$.”

In our work, we model NT-SOA as a set of semi-volatile products. Therefore the change in NT-SOA yields to background OA concentrations is explicitly incorporated into the model.

As the reviewer has pointed out, the smog chamber simulates the real atmospheric oxidation faster. We are not sure how simulating the process faster would influence results.

(7) In Table 1 the authors define the load conditions for the CFM-56 engine with % thrust values. The same rubric should be applied to the T63 engine. This quantification is actually very important given the differences in I/SVOC emissions at low, intermediate and high engine powers. Related to this – the authors define the 7% condition in section 3.1 as “idle/taxing”

Besides the spelling error (should be taxiing) this loose definition leads to further confusion later on in the manuscript. Technically speaking the ICAO specified ground idle engine operating condition is 7% load, so considering 'idle' vs 'non-idle' conditions as much of the subsequent data is presented should classify the 7% data in the idle category. In its present form, the manuscript appears to treat the 7% condition as a non-idle condition.

The different engine modes on the CFM56 have been defined based on a percentage load on the engine (based on N1 fan speed), the test modes for the T63 were defined using the fuel flow rate and engine rpm. Our best guess would be that T63-Idle would be equivalent to the 4% engine load and T63-Cruise would be similar to 60% engine load.

We agree with the reviewer about the 'idle' versus 'non-idle' distinction and subsequent confusion with ICAO terminology. But our work suggests that there are significant differences in emissions, SOA formation and yields between the ground-idle experiments and non-ground-idle experiments. This corresponds to the dramatic increase in VOC emissions at loads less than 7% that have been reported in the literature (Wey et al., 2006). To address that in the text, we have changed 'idle' to 'ground-idle' and 'non-idle' to 'non-ground-idle'.

(8) Figure 2: Given the range of emission ratios for the different species, the Y-axis should be displayed as a log. It is impossible to ascertain the emission ratios for many of the species listed. Also, a legend should be provided.

Although a log Y-axis will help visualize the smaller emissions, it will distort the contributions from the various components. The objective of the figure is to illustrate the contribution of SOA to PM. The legend went missing when various drafts of the manuscript's figures were exchanged between the staff at ACP and us. We have added the legend.

(9) P 9958 Section 3.2: I understand that the purpose of this manuscript is not to give a detailed overview of the aircraft data itself, but the authors should at least describe how the Y-axis in Figure 2 is calculated and the underlying assumptions that are inherent in that calculation. In the caption to figure 2 the authors note that the CFM-56 data is the average of three trials and the T63 data is the average of two trials. At some point in the manuscript the authors should comment on the run-to-run variability for the same operation conditions and how such variability poses challenges to the NT-SOA parameterizations.

The data have already been published in Presto et al., Atmos. Environ., 2011, Miracolo et al., ACP, 2011, Miracolo et al., ES&T, 2012 and Drozd et al., Atmos. Environ., 2012. We have added some detail and changed the text accordingly: "Figure 2 compiles the primary (elemental carbon and primary organic aerosol or POA) and secondary PM (sulfate and SOA) data from the two field campaigns. Briefly, EC and POA emissions were based on quartz filter samples collected off of a dilution tunnel (Drozd et al., 2012;Presto et al., 2011). Sulfate and SOA were based on AMS and SMPS measurements made at the end of ~3 to 4 hrs of photo-oxidation inside the smog chamber (Miracolo et al., 2011;Miracolo et al., 2012). The data are converted to a fuel basis using the background-corrected measured CO₂ concentration."

When compared on an emission factor basis, we do find some variability across the three CFM56-JP8-Ground Idle experiments and the T63-FT-Ground Idle experiments. The variability can be mostly attributed to slight differences in the emissions and some differences in dilution, OH exposure and VOC/NO_x ratio. However, when compared on an SOA yield basis that corrects for differences in dilution, OH exposure and VOC/NO_x ratio, two of the CFM56-JP8-Ground Idle experiments appear very similar while one has a reduced SOA yield (50%). We find that the two FT-Ground Idle experiments are very similar. We expect to see run-to-run variability but will not be able to quantify it for this dataset.

(10) *P 9958 Section 3.3 - Please provide a reference that supports the statement that T63 cruise results in mostly oxygenated species.*

We have not been able to find a reference that shows that and have changed the statement as follows: “Apart from the T63-JP8-Cruise experiment, the measured SOA mass is smaller than the sum of the precursors (S/IVOC + VOC) emissions. Theoretically, the precursor mass would need to be larger than the SOA mass if we believe that the SOA is a product of gas-phase oxidation of organic emissions. It is likely that the precursors in the cruise experiments are mostly oxygenated because our instrumentation largely targets hydrocarbons and modestly polar species.”

(11) *Throughout the manuscript the authors offer a few different definitions of NT-SOA: “SOA formed from POC vapors is defined as non-traditional SOA (NT-SOA). “*

“NT-SOA is defined as the SOA mass formed through the oxidation of unspciated POCs.”

“SOA formed from speciated VOCs is defined as traditional SOA (T-SOA)”

We have corrected the manuscript to reflect a consistent definition, i.e. SOA formed from S/IVOC vapors is defined as non-traditional SOA (NT-SOA).

(12) *The speciated VOC precursors (Table 2) that get incorporated into the T-SOA framework include species that are NOT VOCs such as: C11,C13,C14 n-alkanes. If POCs are defined as the sum of unspciated emissions, it is unclear how the speciated IVOCs are treated in this framework. It appears that all speciated compounds (regardless of volatility) are treated as VOCs and added to the T-SOA totals. Given the importance (as the authors clearly state in the manuscript) of unburned fuel emissions in the C11-C15 IVOC range at engine idle operating conditions, the authors MUST do a better job quantifying and classifying the SOA formed from speciated IVOCs. Getting at the heart of this confusion highlights the issues that may arise from using ‘traditional’ vs ‘non-traditional’ terminology where traditional is tied to VOC precursors only. Given the pace with which SOA models are changing to incorporate I/SVOC treatments, perhaps the authors should consider revising this terminology.*

This work aims to develop a method and associated parameters to model NT-SOA formation in CTMs. Since NT-SOA is defined by difference, i.e. SOA – T-SOA, the NT-SOA parameters are

sensitive to the treatment of T-SOA. Therefore, if we want our NT-SOA parameters to be directly used in CTMs, we need to ensure that our T-SOA model mirrors the T-SOA model in contemporary aerosol models. To address that requirement, our T-SOA model only calculates the SOA arising from speciated VOCs that are typically measured, quantified and accounted in emission inventories and therefore in SOA models. That explains the inclusion of C₁₁-C₁₄ n-alkanes in Table 2. And by definition, the NT-SOA model accounts for both speciated and unspeciated organics that are present in S/IVOC. So, although philosophically it would be much simpler (as the reviewer suggests) to define T-SOA as SOA from speciated organics and NT-SOA as SOA from unspeciated organics, our NT-SOA parameters would not be suitable for direct use in contemporary aerosol models. Further, only a very small fraction of the S/IVOC can be speciated (Presto et al., 2011) therefore, explicitly accounting for them will not significantly change this work's results.

(13) Figure 3. An explanation of how one calculates an average SOA emission factor is warranted. The caption points out the T63 data as the average of two trails but does not mention the multiple trials for the CFM-56. Does this mean that the data shown are just one of the three CFM-56 trails? If so, why was this one run selected over the others?

We made a mistake in the caption. The caption should have read: “The results for CFM56-JP8-Idle are the average of three independent experiments and the T63-FT-Idle are the average of two independent experiments.”.

(14) Figure 4a: Plotting the data as idle and non-idle engine operating conditions is confusing. For example, in the text the authors indicate that the CFM-JP8 takeoff condition needs to be excluded from the comparison in order for ~ 50% of the SOA to be predicted. The upper panel of Figure 4a shows three distinct series of data points for non-idle conditions – it is not clear to the reader if the authors are treating 7% power as idle or non idle given their prior definitions in section 3.1 as mentioned above. Since there are three distinct series of data, I suspect the authors are plotting 7%, 30%, and 85% as non idle. If the authors expect the readers to interpret which engine condition is which in Figure 4a (implied by asking us to not include the takeoff condition when approximating the fractional error) they should use different symbols for each of the different engine power conditions. If the CFM-JP8 take off condition are the data points that lie along the 1:1 line then on average, the two other non-idle conditions do not account for 50% as stated in the text. Overall, it is confusing and somewhat misleading when you ask the reader to ignore a significant amount of data displayed in a graph in order to make a point about the other data included in the graph. At the very least, the authors should provide some justification for the exclusion of the data that fall along the 1:1 line in the T-SOA model approach.

We have changed Figure 4 and 5 (now Figure 5 and 6) to include different symbols and colors to identify different experiments with different engines, engine loads and fuels.

To clarify, the fractional error is calculated using all the data, i.e. no data are excluded. Also, Figure 4 (now Figure 5) plotted total OA (POA + SOA).

Given that different experiments have different proportions of POA, it might not be apparent by just looking at the plot what fraction of SOA was explained by T-SOA. To resolve the issue, we are adding a figure to the supplementary material (Figure S.1) that plots the ratio of T-SOA to measured SOA for all experiments.

Except for the CFM56-JP8-Takeoff and T63-FT-Ground Idle experiments, the T-SOA module predicts less than half of the measured SOA. T-SOA explains most of the SOA measured during the CFM56-JP8-Takeoff and T63-FT-Ground Idle experiments probably because the SOA mass yields of Murphy and Pandis (2010) used to predict T-SOA are at the high end of those reported in the literature.

(15) Regarding the lower panel of Figure 4a – The authors ask us to disregard the FT-Idle data which falls on the 1:1 line. It is not clear why the two Blend-Cruise experiments resulted in 2 orders of magnitude difference in OA emissions. If this is the kind of run-to-run variability that the authors are encapsulating in their averaging routine, how representative of real-world emissions are their results and how does such variability influence the NT-SOA parameterization scheme?

The cruise experiments the reviewer has referred to are two separate experiments using different fuels. They are expected to be different. One is JP8-Cruise and the other is FT-Cruise. The distinction is now clear with the use of different symbols and colors in Figure 4 (now Figure 5).

(16) P9962 L22: “since a lot of the SOA formed in those experiments is explained by T-SOA” The authors need to quantify this statement.

This was a misstatement. It has been changed to: “In comparison, a more modest parameter-set ($k_{OH} = 1-3 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, $f_{oxy} = 0.05-0.3$, $q = 1$) is sufficient to describe the non-idle SOA data.”

(17) Why is it likely that the T63-JP8 cruise emissions are mostly oxygenated species whereas the same is not true for the CFM-56 cruise emissions?

We have corrected our statement to “. Apart from the T63-JP8-Cruise experiment, the measured SOA mass is smaller than the sum of the precursors (S/IVOC + VOC) emissions. The precursor mass should be larger than the SOA mass if the SOA is formed from gas-phase oxidation of organic vapors. The VOC data were of poor quality in the cruise experiments. We hypothesize that these precursors may be mostly oxygenated and therefore poorly detected by the hydrocarbon-focused techniques employed by Presto et al. (2012).”

(18) The authors should consider the role of ambient temperature (air being drawn into the combustor inlet) on the variability of calculated yields of NT-SOA for the same engine operating

conditions.

Unfortunately, all experiments were conducted at roughly the same ambient temperature. So, we could not use our data to answer that question.

(19) In the text, Drozd et al. (2012) should be differentiated from the other publications since it is in preparation.

Drozd et al., 2012 has since been published and updated in the bibliography.

(20) Considering differences in fuel composition and combustion conditions perhaps the authors could comment on how the presented NT-SOA parameterization would differ for biomass, diesel, or gasoline combustion.

It would be very hard to speculate how the NT-SOA parameterization would differ for other combustion systems for two reasons. One, we have very little compositional information about the NT-SOA precursors in aircraft exhaust. And two, there are little SOA data from other combustion systems to compare our work against. In addition, most of the previous work does not try to quantitatively link the SOA formation to emissions. To help answer that questions, we are currently working on another manuscript that examines SOA formation from evaporated fuels (gasoline, JP-8, diesel).

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